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Auger Line Shape as a Probe of
Electronic Structure in Covalent Systems

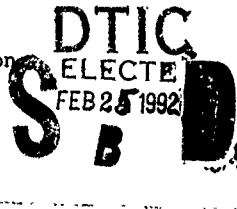
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Auger Line Shapes as a Probe of Electronic Structure in Covalent Systems

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Abstract

Our goal has been to develop a generally applicable, semi-empirical approach for quantitatively interpreting Auger line shapes for covalently bonded systems. In this regard we examine four main topics. First, because the Cini-Sawatzky theory was originally derived for initially filled, single bands in metals, we present our grounds for applying it to covalent systems. Second, we examine the problem of unfilled bands, and third, emphasize the importance of satellites. The role of satellites are examined with regard to benzene, graphite, and the new carbon material, C_{60} , often referred to as "buckyball". Finally we present results of an application to "carbide" carbon on Ni, where fundamental new information was obtained concerning the nucleation of graphite at higher temperatures. In our discussions, results from the interpretation of the C KVV Auger line shapes of five different gas phase hydrocarbons (methane, ethane, cyclohexane, benzene, and ethylene), five different solids (polyethylene, diamond, graphite, "buckyball", and nickel carbides), and a molecularly chemisorbed system (ethylene/Ni) are included.

Our goal has been to build a generally applicable, semi-empirical model for quantitatively interpreting Auger line shapes for covalently bonded systems. This model must have a balanced validity and be relatively convenient to use, so that it can be utilized for a wide variety of materials of technological interest. Our objective is to enhance the suitability of Auger spectral line shape analysis as a source of electronic structure information.

We know that a complete solution of Schrödinger's equation for a two-hole final state in a molecule or cluster gives an excellent interpretation of the Auger line shape. But this approach is inconvenient, and can only be performed on the simplest of molecules. If the interpretation of Auger line shapes is ever going to provide a convenient and useful means of extracting electronic structure information on a wide range of materials, a theory must be provided which is widely applicable, convenient to use, and balanced with regard to its validity and fundamental justification. Considerable progress has been made, but much remains to be done.

After initially presenting our "balanced" theoretical approach, I will examine four topics. More extensive reviews of our work have been published elsewhere [1-5]. In Section 2, I will present our intuitive grounds for applying the Cini-Sawatzky theory to covalent systems. This is important, because the theory was originally derived for initially filled, single bands in metals. In Section 3, I examine the problem of unfilled bands, and in Section 4 the importance of satellites. We examine the role of satellites with regard to benzene, graphite, and the new material, C_{60} , often referred to as "buckyball". In Section 5, I present results of an application to "carbide" carbon on Ni, where fundamental information was obtained from interpretation of the line shape. Section 6 contains a brief summary and

1. A "balanced" theoretical approach

A theoretical prescription for generating the principal kvv component of the Auger line shape can generally be expressed by the equation [6],

$$I_{kvv}(E) = B \Sigma_{ll'} [P_{lll}, R_l R_{l'}, A(E + \delta_{ll'}, \Delta U_{ll'}, \rho_l, \rho_{l'})]. \quad (1)$$

In eqn. (1), the function A is the Cini-Sawatzky function, [7, 8]

$$A(E, \Delta U, \rho, \rho') = \frac{\rho^* \rho'(E)}{[1 - \Delta U I(E)]^2 + [\Delta U \pi \rho^* \rho'(E)]^2} \quad (2)$$

which introduces hole-hole correlation effects, and distorts the DOS self-fold. ΔU is the effective hole-hole correlation parameters and $I(E)$ is the Hilbert transform,

$$I(E) = \int \frac{\rho \times \rho'(\epsilon)}{E - \epsilon} d\epsilon. \quad (3)$$

The Cini function, which distorts the DOS self-fold for treatment of Auger line shapes in solids will be discussed more fully below (Section 2). In eq. (1) we [6, 9-11] have included additional arguments in A to make explicit the point that the total theoretical kvv line shape is a sum of components, with each ll' component (e.g. the ss , sp and pp components or more appropriately each multiplet $2S+1L$) having an energy shift, $\delta_{ll'}$, and a hole-hole correlation parameter, $\Delta U_{ll'}$ (these two parameters are defined more fully in Section 2), and with each component derived from a fold of the ρ_l and $\rho_{l'}$ DOS (e.g. s or p). B is a normalization constant and the R_l 's and P_{lll} 's are core hole screening factors and atomic Auger matrix elements, respectively, to be defined below.

The factors R_l included in eq. (1) are to make the theory consistent with the final state rule for Auger line shapes [12]. The final state rule indicates that (1) the shape of the individual ll' 's contributions should reflect the DOS in the final state, and (2) the intensity of each ll' 's contribution should reflect the electron configuration of the initial state. For the kvv line shape, the final state has no core hole. In general it is assumed that the DOS in the final state and ground state are similar, so that the spectral shape of ρ_l should reflect the ground DOS. However, the initial state in the kvv process has a core hole, therefore the integrated ρ_l should reflect the electron configuration of the initial core hole (CHG) state. The R_l factors are defined,

$$R_l = \int \rho_{CHG}(\epsilon) d\epsilon / \int \rho(\epsilon) d\epsilon. \quad (4)$$

In most systems, the R_l factors are similar so that they are generally ignored. Effectively this ignores the "static" effects of core hole screening. The R_l factors are important only

when one orbital momentum component dominates the screening. This apparently occurs in many metals such as in Li and Be, and in the L_{23} VV line shapes for Na, Mg, Al and Si, where the core-hole screening is dominated by the valence s electrons as opposed to the p electrons. However, considerable disagreement exists as to the dominant screening charge in some systems. For example, Jennison *et al.* [13] on the basis of a semi-empirical theory argue that the core-hole screening involves mainly the s electrons in Be, while recent calculations by Almladh and Morales [14] argue that the p electrons dominate. Recent results [14] also indicate that the total Auger rates calculated from wave functions perturbed by a static core hole are a factor of 2–4 larger than those calculated from ground state orbitals. Thus static core hole screening is important for all Auger processes, but it is known to significantly alter the Auger profile just for certain systems. An analysis of the profile can shed some light on the nature of the core hole screening process.

Consistent with our goal to develop a balanced, consistent, and convenient model, we have utilized empirically determined atomic Auger matrix elements, P_{kl} , and usually an empirical density of states (DOS), ρ , as well. The latter also contains inherent widths, so these are also obtained empirically.

The atomic Auger matrix elements have been calculated for much of the periodic table within a one-electron Hartree-Fock-Slater approximation by McGuire [15] and Walters and Bhalla [16], or in a Dirac-Hartree-Slater approximation by Chen and Crasemann [17–18]. A complete review of calculated Auger transition probabilities has been published [19]. We have shown that the ratios P_{33}/P_{3p} and P_{33}/P_{3pp} for a filled s or p shell (i.e. s^2 or p^6) are remarkably constant with Z , the atomic number. However, comparison with experimental ratios reveal that electron correlation effects dramatically alter these ratios (by factors of two or more) so that the one-electron results are inadequate for use in line shape analyses. Therefore, either electron correlation must be included, such as by performing a configuration interaction (CI calculation) or the one-electron results must be scaled [5, 20]. For all carbon compounds we used $P_{33} : P_{3p} : P_{3pp} = 0.8 : 0.5 : 1$ [6].

A basic concept in AES concerns the nature of the density of states (DOS) reflected in the line shape. First, it is well-known that AES samples a site specific DOS, i.e. the DOS specific to that atomic with the initial core hole. A self-fold of the appropriate one-electron density of states (DOS) on this site, $\rho^*(E)$,

$$\rho^*(E) = \int \rho(E - e) \rho(e) de, \quad (5)$$

then represents a first approximation to the line shape [21]. Hence, almost all line shape analyses start with a determination of the one-electron DOS.

We have often used an empirical procedure to obtain the DOS. Photoelectron spectroscopy (x-ray or ultraviolet, XPS or UPS) is often used independently or a combination of x-ray emission (XES) and XPS, along with theoretical calculations. Furthermore, many of the molecular orbitals (MO's) in alkanes have primarily either carbon-carbon (C-C) or carbon-hydrogen (C-H) bonding character [22] or σ or π character for the alkenes. In the Auger spectrum, it has

been shown previously [23] that final states involving these different MO's have different hole-hole repulsions. Therefore, the p DOS must be separated in the p_{CC} and p_{CH} or p_σ and p_π components. We have given prescriptions for doing this previously [24, 6].

Several arguments can be given for utilizing semi-empirically derived DOS, even for simple molecules [6]. First, most one-electron theoretical calculations do not include electron correlation effects and therefore do not give sufficiently accurate binding energies. Second, the semi-empirical DOS include approximate widths for each orbital feature. Assuming the XES and XPS spectra utilized to obtain the DOS were measured at sufficiently high resolution, these widths primarily reflect broadening due to the vibrational state manifold of the final state which project onto the core initial state in XES, or the ground state in PES. The DOS self-fold, $\rho^*(E)$ then has twice the vibrational broadening consistent in first approximation with the Auger two-hole final state.

Matthew has determined that if the core lifetime is much less than a vibrational period, and if the electron-phonon coupling and linear dielectric response are linear, then the widths for photoemission and Auger processes are comparable for the case of localized holes in ionic crystals [25]. On the other hand, for rare gases physisorbed on metal surfaces, the Auger width (FWHM) will be about 3 times greater than the PES width. Other accurate calculations for the O_2 molecule indicate that the Auger width is about a factor of 2 greater than the PES width (i.e. that a PES self-fold is a reasonable approximation to the Auger widths) [26]. Thus the self-fold of PES or XES data may not accurately reproduce the Auger widths, but it appears to be a good first approximation to them, at least for molecules when vibrational broadening dominates.

It is important to include the vibrational widths of the various orbital states for a quantitative interpretation of experimental spectra, at least for molecules. Often sophisticated techniques are utilized to obtain the one-electron DOS, without considering the vibrational widths. After calculating the energies and intensities by theory, a bar diagram (i.e. zero widths) is then compared with the experimental data. Sometimes a constant broadening of all lines is utilized. Using these procedures, the presence of satellites sometimes has not even been recognized, particularly when the normal k_{VV} line shape accounts for all the major features.

The above gives a summary of what is meant by a "balanced" approach. To obtain an accurate theoretical many-body DOS, but then to ignore the widths, or to use the one-electron atomic matrix elements, makes the effort in obtaining the accurate DOS fruitless. To extract meaningful information from the Auger line shape, reasonable DOS, widths, and atomic matrix elements must be utilized. We have most often obtained these empirically along with strong theoretical support.

2. The Cini-Sawatzky model for covalent systems

The Cini-Sawatzky model has been the basis for understanding correlation effects in Auger line shapes. In elemental solids, two parameters determine the degree of localization of the CVV (core-valence-valence) two-hole

final state. If the effective Coulomb repulsion U_{xx} is large compared to the band width ($U_{xx} > \Gamma$), the line shape will be atomic-like, if $\Gamma < U_{xx}$, the line shape will be band-like. In systems where $U_{xx} \approx \Gamma$, both atomic- and band-like contributions are evident in the line shape (i.e. correlation effects are important [7, 8]).

The results of Cini and Sawatzky were obtained from utilizing the Anderson and Hubbard many-body models. The Cini expression was derived assuming an initially filled single band so that it is not rigorously valid for partially filled bands or degenerate bands [7]. Nevertheless, the Cini-Sawatzky expression, in the absence of a better alternative, has been used for metals, alloys, and insulators, and even molecules (i.e. systems for which the bands are not filled and which have degenerate bands), with apparently satisfactory results.

The Cini-Sawatzky results can be simply understood by considering a cluster LCAO-MO-Cl technique where molecular orbitals (MO's) are constructed and mixed in a configuration interaction (CI) [27]. For the moment consider a simple two orbital system which has two holes present resulting from the Auger process in an initially filled state [28]. The holes can be described by one-electron molecular orbitals $\phi_a = N(f_1 + f_2)$ and $\phi_b = N(f_1 - f_2)$ (bonding and antibonding molecular orbitals constructed from \pm linear combinations of atomic orbitals, f_i on atom 1 or 2) with binding energy $\epsilon + V$ and $\epsilon - V$ ($\epsilon = \langle f_1 | H | f_1 \rangle$ and $V = \sqrt{2} \langle f_1 | H | f_2 \rangle$ where V is called the covalent interaction and H is the proper Hamiltonian operator). This gives the Hamiltonian matrix as follows:

$$\begin{vmatrix} \phi_a^2 & \phi_b^2 \\ \phi_a^2 | 2\epsilon + V + \delta & U_{11} - U_{12} \\ \phi_b^2 | U_{11} - U_{12} & 2\epsilon + V + \delta \end{vmatrix} \quad (6)$$

where $U_{11} = \langle f_1^2 | r_{12}^{-1} | f_1^2 \rangle$ and $U_{12} = \langle f_1 f_2 | r_{12}^{-1} | f_1 f_2 \rangle$. Clearly if $V < U_{11} - U_{12}$, very little mixing occurs and the hole state M.O.'s ϕ_a and ϕ_b properly describe the localization of the two holes. In this instance the Auger line shape is molecular-like. If $V \gg U_{11} - U_{12}$, the mixing of the configurations is complete and the linear combination $\phi_a^2 \pm \phi_b^2 \approx f_1^2$ or f_2^2 properly describe the localization of the holes. As such, the line shape is atomic-like and gives Auger intensities reflecting the DOS on the atom with the core-hole. If $V \approx U_{11} - U_{12}$, of course intermediate mixing occurs giving both contributions.

For metallic behavior, U_{12} , will be drastically reduced by electron screening, so that $\Delta U \approx U_{11}$. For extended systems, the parameter δ goes to zero. This is the essence of the Cini-Sawatzky expression, eq. (2).

Dunlap *et al.* have generalized these concepts to multi-element covalent systems by providing criteria,

$$\begin{aligned} \text{AO: } & V < \Delta U_{xx}, \\ \text{BO: } & V > \Delta U_{xx}, & < \Delta U_{bb}, \\ \text{GO: } & \gamma > \Delta U_{bb}, & \Gamma < \Delta U_{xx}, \\ \text{EBO: } & \Gamma > \Delta U_{xx}. \end{aligned} \quad (7)$$

for assessing the nature of localization in covalent systems where intermediate levels of localization can occur [28]. In these systems the localization can occur onto atomic, bond, group or extended band orbitals (AO, BO, GO, or EBO).

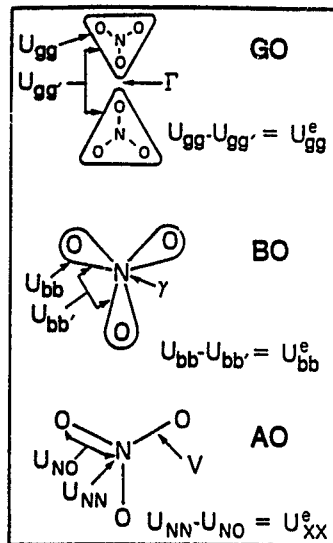


Fig. 1. Illustration of the effective hole-hole repulsions U_{xx} , U_{bb} and U_{xx} [$U^e = \Delta U$ in eq. (2)] and the corresponding interaction parameter, Γ , γ , or V for the NO_2 anion. GO, BO, and AO refer to group (or cluster), bond and atomic orbitals, respectively.

Here V is the covalent interaction between nearest neighbor AO's and can be estimated from the bonding-antibonding orbital energy separation. γ is the covalent interaction between nearest neighbor BO's and can be estimated from the s and p atomic orbital energy separation. Γ is the covalent interaction between neighboring GO's; for example, the GO's are the planar arrangement of three N-O BO's about a single N atom. (In metals, the extended band width is determined primarily by V , but more commonly the symbol Γ is used to refer to the extended bandwidth. Consistent with this, Γ is used in the previous section to refer to the bandwidths in metals.) U_{xx} , U_{bb} , and U_{xx} are the effective Coulomb interactions between holes localized on a single AO, BO or GO, respectively, and are schematically defined in Fig. 1.

To intuitively understand this intermediate level localization phenomena consider Fig. 2. Figure 2, utilizing a schematic one-electron DOS, illustrates the covalent parameters V , γ , and Γ and the application of eq. (1) with increasingly larger values of U . $\rho^* \rho$ in Fig. 2(b) is representative of the Auger line shape provided the σ , σ^* , π , and π^* bands are all filled and all localization effects are negligible, i.e. $\Delta U = 0$. Figures 2(c)-(f) show clearly that distortion effects on each subband are reasonably independent of the other regions of the spectrum until U is sufficiently large to encompass these other regions. For $U = 0.1-1.5$ eV, no significant distortion effects occur indicating the EBO's best describe the final state holes. For $U = 1.5-2.5$ eV, the various ll' ($ll' = ss, sp$, etc.) subbands are distorted into narrower resonance-like features indicative of localization onto single GO's. $U = 2.5-4$ eV causes mixing of bands with bonding-antibonding character and demonstrates localization onto group or atomic orbitals (AO's). If the interaction U is

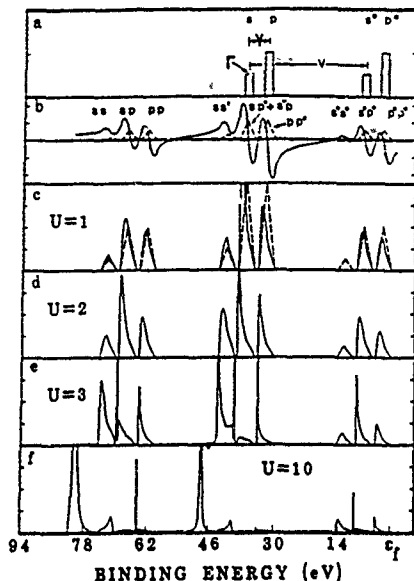


Fig. 2. (a) Schematic one-electron DOS, ρ , and an illustration of Γ , γ , and V as defined in Fig. 1. Here $\Gamma = 2\text{eV}$, $\gamma = 5\text{eV}$ and $V = 30\text{eV}$. (b) Comparison of ρ^*p (dashed line) and the Hubert transform, $I(E)$ (solid line). (c)-(f) Comparison of ρ^*p (dashed line) with $A(E)$ (solid line) obtained from utilizing eq. (2) with the U 's indicated

are empty, as in most covalent systems, localization onto the atomic orbitals will not occur because the mixing in of empty orbitals means the final state holes are being screened by other electrons and hence the effective U is decreased.

Now consider diamond. It is well known that the best starting point for considering the occupied DOS in diamond is to consider a linear combination of bond orbitals, since the bonding and antibonding σ bands are so far removed in energy from one another (they are separated by a large band gap). Thus, we can say at the outset that $\Delta U_{ss} < V$ (the AO-AO interaction parameter), and we will not have atomic localization such as that seen in the metals discussed above. What about BO localization? The one-electron DOS for diamond has the s and p dominated peaks separated by more than 10eV [29]. These s and p DOS arise from the clustering of four bond orbitals about each C atom having s and p symmetry (actually a_1 and t_2 symmetry in the point group for tetrahedral symmetry, T_d). If the s and p bands can be treated as separate bands, i.e. $\Delta U_{pp} < \gamma$ (the BO-BO covalent interaction parameter), then we do not have BO localization. This leaves us with GO localization, which is proposed for diamond.

We can state this in another way. When the $2s+1L$ multiplet contributions arising from the GO's are resolved sufficiently so that separate features are visible, we can speak of BO localization, since these separate features then correspond to configurations of holes on the same or different BO's. When the multiplets are not sufficiently resolved we speak of GO localization. In this case, the same $2s+1L$ multiplets arising from different bands decouple, and the

bands can be treated independently [e.g. the $ss(1S)$ and $pp(1S)$ multiplets decouple]. Furthermore for small U 's, the different $2s+1L$ multiplets arising from the same band apparently can be averaged together to give an effective ss , sp , and pp contribution (e.g. the $1S$ and $1D$ multiplets from the pp contribution can be summed before applying the Cini expression).

We can generalize this picture for the hydrocarbons. Examination of the wavefunctions for most hydrocarbons show that the MO's can best be considered as linear combinations of CH_x GO's [22]. It follows that for most of the C based systems, GO localization is the best qualitative picture for characterizing the localization.

Analysis of the Auger profiles and bonding in covalent systems indicates that a correlation exists between the ionic bonding character and the nature of the localization. As the bond orbitals polarize from say atom N to O in an NO_3 type cluster in Fig. 1, U_{bb} increases, and γ decreases. The increase of U_{bb} relative to γ raises the extent of BO localization. We conclude that increasing BO ionicity increases the character of the localization from GO to BO. Thus the more ionic BeO , [30] BN and B_2O_3 [31] solids can best be characterized as exhibiting BO localization. The silicon tetrahalide molecules, SiX_4 , exhibit BO localization, consistent with the large Si-X electronegativity difference, in contrast with CF_4 , which does not, consistent with the smaller electronegativity difference here [32]. The oxyanions NO_3^- [33], PO_4^{3-} and SO_4^{2-} , regardless of cation, exhibit GO localization [28]. In this latter case, it is expected that the holes cannot get off the oxyanions where they were created by L_{23} VV process, so that GO localization is a fair accomplishment. The Si L_{23} VV profile for SiO_2 exhibits structure similar to that for the SiX_4 molecules, so that it also appears to exhibit some BO localization character [27].

The application of the Cini expression to the empirical DOS for molecules is another approximation requiring further justification. This is problematic since the empirical DOS contain the vibrational broadening which has nothing to do with the correlation problem. However, vibrational broadening is also present in the empirical DOS for solids; it just is not as evident since banding effects dominate. Extended covalent solids contain banding effects which also do not dictate the correlation. To illustrate this, let us consider the DOS for benzene with that for graphite. The local sp^2 bonding around each C atom is essentially the same and this is reflected in the similar gross features in the DOS. The small differences arise because vibrational effects dominate in benzene while banding effects (i.e. second, third etc. nearest neighbor interactions) dominate for graphite. However, the principal correlation effects are determined by the local bonding. Thus neither the extended banding effects in graphite nor vibrational effects in benzene (both broaden the major DOS features) determine the correlation distortion. It has been shown that the Cini expression mimics the effects of a configuration interaction for molecules. Thus, we intuitively expect that the Cini expression has comparable validity for molecules and covalent solids. This is true provided the separation, ΔE , between the molecular levels is small compared with the vibrational broadening, ΔV . This does appear to be true for the molecules such as benzene, hexane, and larger molecules, but may not be appropriate for ethylene, etc. involving three or less carbon atoms. In

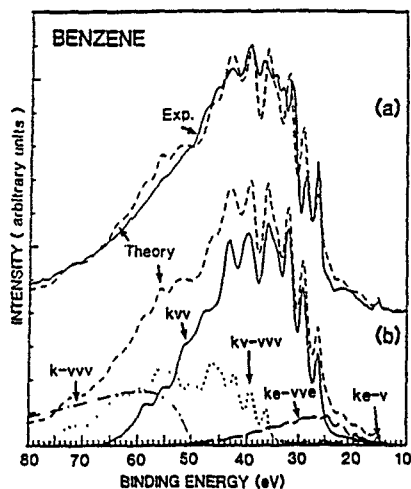


Fig. 3. (a) Comparison of the C KVV experimental [34] and theoretical Auger line shapes for benzene (from Ref. [6]). (b) The total theoretical line shape and each of the components as indicated. The various contributions (kvv, kv-vvv, k-vvv, ke-v, ke-vv) were obtained as described in the text, and having ΔU 's and relative intensities as indicated in Tables I and II.

these smaller molecules, multiplet, are also more important, so that this approach is certainly not completely satisfactory for these small molecules [6].

Figures 3 and 4 compare the optimal total theoretical line shape with the experimental line shapes for ethylene and benzene [34]. In general, the theoretical line shapes generated by the formalism described agree nicely with the experimental line shapes. Similarly good agreement is obtained for other gas phase molecules not shown, i.e., for methane, ethane and cyclohexane [6]. Table I summarizes the ΔU and δ parameters for the principal kvv components.

Comparison of the ΔU 's for molecules and extended solids in Table I indicates something about the nature of the screening processes in these covalent systems. Note that the ΔU for the CC-CC contribution increases in the order cyclohexane < polyethylene < diamond. This can be under-

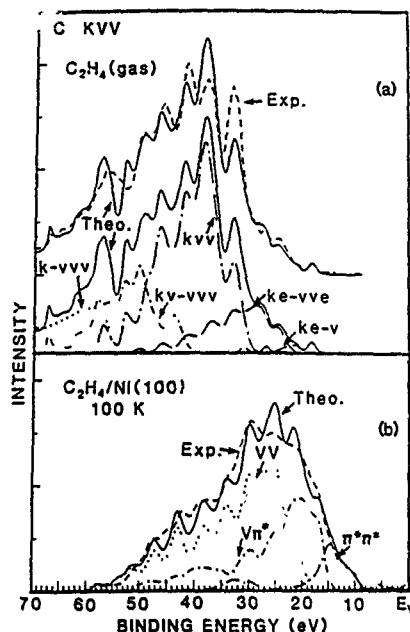


Fig. 4. (a) Same as for Fig. 3 but for ethylene gas [34]. (b) Comparison of the experimental and theoretical Auger line shapes for ethylene chemisorbed on Ni(100) at 100 K (π -bonded ethylene). The three component (VV, Vn*, n*n*) line shapes were obtained as described in the text and in Ref. [63]. The relative intensities were obtained by least squares fit to the experimental data. (From Ref. [63]).

stood from the definition of $\Delta U = U_{11} - U_{12}$. For very short screening lengths, one might expect both U_{11} and U_{12} to be reduced substantially, so that ΔU would be decreased [10]. For long screening lengths, one might expect U_{12} to be decreased more than U_{11} , having the effect of increasing ΔU . Apparently the latter is occurring in these materials. The longer chain length in polyethylene and full three dimensional covalency in diamond suggests that the extent

Table I. Summary of ΔU and δ parameters obtained empirically for the theoretical kvv line shape*

Molecule	ΔU (eV)			δ^a (eV)		
	CH-CH	CH-CC	CC-CC	CH-CH	CH-CC	CC-CC
Alkanes						
Methane	0			12		
Ethane	1	1	0	12	10	10
Cyclohexane	3	3	1.25	9	9	9
Polyethylene	3	3	1.25	0	0	0
Diamond			2			0
Alkenes	$\sigma\sigma$	$\sigma\pi$	$\pi\pi$	$\sigma\sigma$	$\sigma\pi$	$\pi\pi$
Ethylene	2	1	0	9	11	11
Benzene	2	1	0	8	6	6
Graphite	2	1	0	0	0	0
"Buckyball"	2	1	0	0	0	0

* From Ref. [61]

of polarization should increase in the order cyclohexane < polyethylene < diamond. This increased polarization then has the effect of increasing ΔU . For the alkenes, the ΔU 's are all the same. This suggests that the screening length is much shorter so that "full" screening already occurs in ethylene. This is consistent with the more delocalized π electrons in the alkenes.

The δ parameters in eqs (1) and (6) are interpreted as the delocalized hole-hole repulsion [6, 28]. As the size of the molecule increases, Table I shows that δ decreases, reflecting the ability of the two final state holes to stay apart from each other in the delocalized molecular orbitals. Note also that for similar sized molecules, the δ 's for the alkenes are smaller than for the alkanes. This may reflect the increased screening due to the π electrons. Note that the δ 's are zero for the extended solids, as expected, although a controversy has existed for polyethylene (the problem has arisen from energy calibration problems which will not be discussed here [35, 36]).

Cini has recently applied the BLA theory (to be discussed briefly in the next section) along with the full multiplet and intermediate spin-orbit coupling theory, without further simplifying assumptions, to the C KVV line shape of graphite [37]. The theoretical line shape he obtained was amazingly similar to that obtained empirically by us [10], when we ignored the multiplet decomposition and applied the Cini expression directly to the full ss to the ss , sp and pp contributions [10]. It seems clear that the approximations discussed above are indeed valid for these carbon based systems when the correlation effects are not too dramatic. Although the theoretical line shapes obtained by Cini and us were nearly the same, the resultant U 's were very different. We initially found U 's of 0.6, 1.5 and 2.2 eV for the $\pi\pi$, $\sigma\pi$, and $\sigma\sigma$ components [10] (in a slightly different procedure we [6] obtained the values in Table III namely 0, 1, and 2 eV), while Cini found values of 5.5, 11 and 11 eV. What can account for these dramatically different U 's but with the same line shape? The ΔU 's reported in Table I are interpreted as $U_{ss} - U_{ss'}$, i.e. appropriate for group or cluster orbitals as discussed above, and these values are reasonable in this context. I suspect the U 's reported by Cini represent the single center U_{11} on a single carbon atom or cluster orbital, and thus are also reasonable. Nevertheless more theoretical work needs to be done here to more fundamentally understand the U parameters obtained for highly covalent systems.

3. The problem of unfilled bands

Within the approximation discussed above, covalently bonded systems generally have initially filled bands. This is particularly true for the σ bands, which are generally far removed from the π bands. On the other hand, the separation between the π and π^* bands is much smaller, so that the π and π^* bands together may have to be treated as a single band. In this case the π band is half-filled in the initial state, and many additional complications enter. Sawatzky has presented a simple illustration for nearly half-filled bands showing that the usual theory is totally inadequate for highly correlated systems in this case, and that even

Some theoretical work has been reported for initially unfilled bands by Treglia *et al.* [38], Cini *et al.* [39-41] and Liebsch [42]. We briefly summarize some of this work. According to Treglia *et al.*, the Cini equation is still applicable for nearly filled bands (i.e. low hole density); however, $\rho(E)$ must now include the self-energy effects. In this prescription, $\rho(E)$ might be determined from the measured photoemission spectrum which includes static and dynamic screening effects, etc. (the latter introduces satellite contributions) [43]. Cubiotti *et al.* [44] applied the model of Treglia *et al.* to consider the XVV spectra of several alloys; unfortunately, they did not compare their results with experiment to verify their findings. However, Cini *et al.* suggest that within the ladder approximation, the undressed or bare one-hole propagator is more appropriate (this has become known as the bare ladder approximation, BLA) [41]. Cini has concluded for Pd [40] and graphite [37], both possessing unfilled bands, that the Cini expression can satisfactorily be utilized with the undressed DOS, provided ΔU is treated as a parameter to give an optimum fit to experiment, and the correlation effects are small. Apparently, the two holes tend to interact more as bare holes because the size of their screening clouds is larger than the range of hole-hole repulsion. Bennet *et al.* [43] have introduced a procedure which removes any photoemission satellite contributions so that the undressed DOS might be approximated empirically assuming the remaining static screening effects are relatively small. We believe that Cini's bare ladder approximation is, at last qualitatively, able to handle all situations. Treglia's approximation may also be adequate provided the satellite contributions are removed. Which of these approaches is better is however not yet clear.

To intuitively understand some of the additional complications which arise for half-filled bands, and how negative U 's may enter, we consider again the simple diatomic molecule as in eq. (6) above, and compare the case when the band is initially full on the left and when the band is half full on the right:

	Full	Half full
Initial state	$\phi_1^2 \phi_2^2$	ϕ_1^1
Final state	$\phi_1^1 \phi_2^1$	empty
Matrix element	$\langle 1s k \rangle r_{12}^{-1} \langle \phi_1 \phi_1 \rangle$	$\langle \phi_1 \phi_1 r_{12}^{-1} 1s k \rangle$

(8)

The $1s$ and k refer to the core and continuum orbitals involved. The Auger matrix can be written in either the hole picture or the electron picture; i.e. we can enumerate the electrons or the holes. Obviously, on the left, it is better to consider the holes, while on the right better to consider the electrons, because in either case we then have an empty band; empty of holes in the initial state on the left, and empty of electrons in the final state on the right. Therefore, we need to worry only about final state hole-hole interaction on the left, and initial state electron-electron interaction on the right. This initial state electron interaction on the right will increase the initial state energy, thus increasing the Auger kinetic energy, and make the conventional U parameter come out negative. For $U > W$, the two electrons will remain on separate atoms (antiferromagnetic), and the Auger intensity goes to zero for less than one-half filled

both the intensity and the profile. This is to be expected, since by the nature of the sum rules, the initial state must always determine the total intensity [12].

We have previously applied these intuitive ideas by utilizing the Cini expression as depicted in Fig. 5 where the final state and the initial state rule prescriptions are compared [45]. In the initial state prescription, appropriate for less than or equal to half-filled bands, the Cini expression is applied to the entire DOS, occupied and unoccupied portions. As U increases the occupied DOS self-fold is distorted upward by a negative U and the total Auger intensity (shaded area) decreases. This is in contrast to the final state case, where the distortion is downward, and the total intensity is conserved because it is applied only to the occupied part. The upward distortion in the less than half-filled case occurs because the Auger process tends to select those electrons which exist on the same atom in the initial state.

Evidence for negative U effects have indeed appeared in the Auger lineshape of covalent systems involving the π bands. The $\pi\pi$ Auger contribution for the benzene molecule shows an upward distortion [45]. It is believed this arises because the total π band (bonding plus antibonding) is half filled in benzene and hence a negative U is appropriate within the initial state rule. Ramaker also has shown that the $\pi\pi$ contribution arising from the reconstructed clean diamond surface within Pandey's π -bonded chain model can be explained by a negative U , which strongly reduces the $\pi\pi$ contribution vs. the $\sigma\pi$ coming from the surface [11]. Finally, some very interesting correlation effects have been observed in core EELS spectra for Ti and V metals which suggest similar effects [46].

The existence of negative U 's has also been observed for the transition metals on the left side of the periodic table, i.e. with less than half-filled 3d bands. Indeed, the U becomes increasing negative as the band becomes more unfilled [47]. Negative U 's have also been found for some transition com-

pounds, such as CrSe_2 and TiSe_2 [47]. Different suggestions have been given to account for these negative U 's. DeBoer *et al.* [47] suggested that the negative U 's were caused by a dynamic bipolaron effect involving the conduction electrons. Others have proposed that these are caused by the potential of the core-hole in the initial state, i.e. due to edge or non-orthogonality effects [48, 49]. Ramaker *et al.* have argued that for the low electron density limit, i.e. nearly empty bands, the negative U values can be interpreted as arising naturally from correlation effects in the initial state as discussed above [45, 46].

We can summarize these intuitive discussions as follows [1]:

(a) The final state (i.e. ground state for CVV processes) DOS is the most appropriate one in nearly all cases.

(b) It is best to use the uncorrelated DOS, or the correlated DOS but without the satellite contributions. Agreement on which of these is best has not yet been obtained.

(c) For nearly filled bands, the Auger profile apparently reflects the multiplets from hole-hole coupling in the final state that gives the usual positive U 's.

For significantly less than half-filled bands, the Auger profile reflects the multiplets of the electrons in the initial state, that gives negative U 's in the usual sense.

(d) The initial state determines the total intensity in all cases. For less than half filled bands, electron-electron coupling is critical to determining this intensity.

It seems clear that much more rigorous work is required to sort out these complicated correlation and screening effects for initially unfilled bands. We anticipate much more work in this critical area in the near future.

4. The importance of satellites

The presence of satellite contributions in the Auger spectra of molecules and free atoms has been known for some time, but their importance (at least in solids) has been recognized only relatively recently [6, 50-54]. It has been shown that the processes producing these satellite contributions are resonant excitation, initial-state shakeoff and shakeup, and final-state shakeoff and shakeup [6].

The process creating each satellite in the lineshape is illustrated in Fig. 6. The notation indicates the particles in the initial and final states before and after the hyphen [6]. Here, the "k" refers to the initial 1s core hole, the "e" to the resonantly excited bound electron, and v or π to a general valence (or more specifically π -valence) hole created either by the "shakeup" or "shakeoff" process or by the Auger decay. The principal Auger process is indicated without the hyphen (kvv rather than k-vv) consistent with that used historically. We use kvv to indicate this principal or normal Auger contribution to differentiate it from the total KVV experimental line shape.

In Fig. 6 ke-vve refers to the resonant Auger satellite. It arises when Auger decay occurs in the presence of a localized electron, which was created by resonant excitation into an excitonic or bound state upon creation of the core hole. The ke-v contribution arises when the resonantly excited electron participates in the Auger decay. The kze-vve and kze-vv satellites arise from initial state shake-up followed by

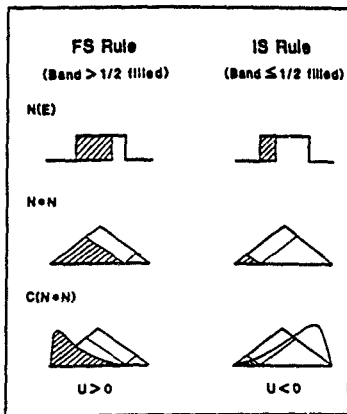


Fig. 5 Schematic illustration of the final (FS) and initial (IS) state rules applied to a single-band rectangular DOS, $N(E)$, with greater and less than half filled valence bands respectively. The DOS self-fold N^*N and the Cini

HOMO	Res. excit.		Shakeup		Shakeoff	
	excit. only	excit.	excit.	excit.	excit.	excit.
	spec.	part.	spec.	part.	spec.	part.
kvv	ke-vve	ke-v	ke-vve	ke-v	ke-vve	ke-v
CB						
VB						
Core						
	U	< U	-ΔE	U	U	-ΔE
Benzene	ΔU/2,1,0	yes	yes	n.e.	n.e.	yes
Graphite	ΔU/2,1,0	no	no	n.e.	yes	no
C ₆₀	ΔU/2,1,0	no	no	yes	yes	n.e.

Fig. 6 Summary of the various processes giving rise to the total Auger line shape. Core, VB, "c" and CB indicate the core level, valence band (or filled orbitals), "excitonic" (usually π^*) electron orbital, and conduction band (or empty orbitals) respectively. Spec. (spectator) and part. (participant) indicate the subsequent fate of the resonantly excited electron during the Auger process. Is. and fs. indicate initial-state and final-state and refer to the state in which the shakeoff event occurs relative to the Auger decay. N^*N and N [$N = \rho$ in eq. (1)] refer to the approximate line shape, i.e. either a DOS self-fold, or just the DOS, with the relative size of ΔU in the Cini expression [eq. (2)] indicated. The resonant satellites occur only under electron excitation. At the bottom, the presence (yes) or absence (either definitely not present (no) or not evident (n.e.)) of each satellite is indicated for benzene, graphite, or C₆₀. The presence of a small k-vvve satellite for graphite is indicated but not clear.

shake-up upon filling the core hole during the Auger process. The kv-vvv satellite arises when Auger decay occurs in the presence of a localized valence hole, which was created via the shakeoff process during the initial ionization. The shakeup or shakeoff of a valence electron is an intrinsic phenomena resulting from the "sudden" change of the core hole potential upon ionization. The k-vvv term denotes the final state shake Auger satellite, which arises when Auger decay occurs simultaneously with shakeoff of a valence hole. These latter five terms arise as a direct result of core hole screening. The ke-vve and ke-v terms arise because the Auger process is generally excited by electron excitation which allows the resonant excitation.

In light of the above, the line shape apparently consists of the sum of several intensities, namely that of the principal kvv contribution plus several satellites. The relative intensities of the satellites are generally obtained by least squares fit of the several line shapes to the experimental spectra [6, 50]. The results for benzene, ethylene, and C₆₀ are shown in Figs. 3, 4 and 7, respectively. The results in Fig. 4 for ethylene and the conclusions concerning the importance of satellite contributions utilizing the semi-empirical method is totally consistent with recent ab-initio Green's functions results reported by Ohrendorf *et al.* [55].

Figure 6 schematically indicates how we generate the line-shape for each satellite and compares the presence of these satellites for benzene, graphite, and C₆₀. Table II summarizes the intensities of each satellite for all the carbon systems studied. In Fig. 6, N^*N indicates the normal DOS self-fold weighted with atomic matrix elements and with the optimal U 's and/or δ 's included [i.e. eq. (1) with the U 's and δ 's in Table I].

The ke-vve lineshape also reflects a DOS self-fold but

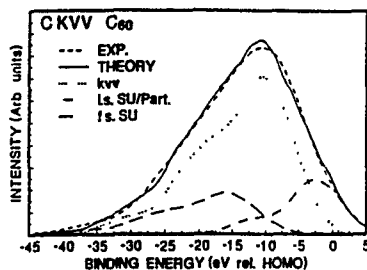


Fig. 7. Comparison of the C KVV experimental and theoretical Auger line shapes for C₆₀. (From Ref. [56].) The ke-vv (fs, SU/part.) and k-vvve (fs, SU) satellites were shifted by +5.5 and -5.5 eV respectively consistent with that indicated by the C 1s XPS data [60]. The relative intensities are given in Table II.

holes. The ke-v lineshape in contrast reflects directly the DOS; however, shifted by the binding energy of the excited electron [6]. The resonantly excited satellites appear only with electron excitation, and are clearly present for ethylene and benzene (Figs. 3 and 4). They do not appear in graphite or C₆₀ because the resonantly excited electron propagates away from the core hole before the Auger decay. This is evident from comparison of the electron excited and x-ray excited Auger lineshapes, which are identical for graphite [10] and C₆₀ [56-58], but not for benzene [6].

The initial and final state shakeup satellites enter with large intensity for C₆₀. They are not evident in benzene nor the alkanes, because the shakeup probability is significantly smaller, as indicated by the C 1s XPS spectra, and because at least for benzene, the resonantly excited contributions are larger and appear in the same energy region. The ke-vv satellite appears in graphite, but only with small intensity, and only from shakeup right near the Fermi level (i.e. excitation of electron-hole pairs across the negligibly small band gap) [59]. The higher energy π to π^* excitations are apparently not sufficiently localized in graphite to cause a satellite, but they do appear quantitatively in C₆₀. C 1s XPS data reveals a shakeup satellite of about $15 \pm 10\%$ with a shakeup energy around 5.5 eV for C₆₀ [60]. Simple calculations reveal that this electron should participate in the Auger decay about 47% of the time giving a theoretical estimate for this satellite intensity of 0.06 in ~~good~~ agreement

Table II. Summary of satellite intensities in percent^a

	kvv ^b	ke-v	ke-vve	ke-vv	k-vvve	kv-vvv	k-vvv
Methane	51	0	12	0	0	20	17
Ethane	52	0	12	0	0	21	15
Cyclohexane	54	0	8	0	0	19	19
Polyethylene	67	3	11	0	0	17-21	0
Diamond	100	0	0	0	0	0	0
Ethylene	50	2	13	0	0	20	15
Benzene	56	1	5	0	0	21	16
Graphite	93	0	0	7 ^c	0	0	0
"Buckyball"	67	0	0	16	18	0	0

^a From Ref. [6].

^b Includes intensity of ke-vvve satellite which has same lineshape.

with that found experimentally (Table II). Furthermore, the final state shakeup k-vvve satellite should then appear with 0.23 intensity [0.15*(1 - 0.85)], slightly larger than the 0.08 found experimentally.

We note that the relative intensities of the kv-vvv satellites for the 6 molecules listed in Table II are essentially all around 20% to within experimental error [6]. Methane is isoelectronic with the neon atom. The shakeoff probability for neon has been both measured and calculated to be around 21%. This is in excellent agreement with that found for all of the carbon systems [61, 62]. Table II shows that the empirically determined intensity for the k-vvv satellite is quite constant around 17% in close agreement with that expected theoretically [i.e. $0.21*(1 - 0.21) = 0.17$].

The kv-vvv satellite does not appear in graphite, diamond, and C_{60} , because the shakeoff valence hole is not sufficiently localized to witness the Auger decay [10, 11, 56]. In the presence of a core hole, the occupied valence band DOS of diamond indeed does not exhibit any bound states [9]. On the other hand, the DOS for polyethylene in the presence of a core hole does exhibit narrow peaks indicative of bound-like states, consistent with the kv-vvv satellite observed for polyethylene. The k-vvv final state shakeoff satellites are not evident (although surely present) for the solids because these are removed along with the extrinsic loss contributions in the deconvolution process utilized to generate the lineshape.

In summary the correlation effects in benzene, C_{60} , and graphite are the same. The $1s^{-1}\pi^*$ resonant and $1s^{-1}v^{-1}$ shakeoff excitations are delocalized in times short relative to the core level width in both graphite and C_{60} ; however, the $1s^{-1}\pi^{-1}\pi^*$ shakeup excitation is localized in C_{60} , but not graphite. Finally no evidence exist for local spin ordering of the π electrons in C_{60} , as seen on the surface of diamond (see Section 3). We might have expected this because of the reduced non-planar p-p interaction in the π band of C_{60} , but apparently this reduction is not significant [56].

5. Molecular adsorbates

Once a molecule is placed on a metal surface, localization of the hole on the molecule is no longer a *fait accompli*. The hole can escape via electron transfer from the substrate, i.e. charge transfer. It is therefore interesting to compare the Auger spectrum for the free molecule with that for the molecular adsorbate.

We consider in detail here the results for ethylene/Ni at 100 K. Figure 4 compares the Auger line shape for gas phase C_2H_4 with C_2H_4 /Ni at 100 K (i.e. for π -bonded ethylene) [63]. The spectrum in Fig. 4(b) was excited by x-rays, so that no resonant satellites appear. Charge transfer from the substrate into the π^* orbital occurs to screen the holes, in both the core-hole initial state and the two- or three-hole Auger final state. This charge transfer has the affect of decreasing the ΔU and δ parameters; the transferred charge playing the role of the resonantly excited electron in the gas phase [63]. Thus the kvv and kv-vvv contributions which comprise the intramolecular component (i.e. termed the VV component) for the chemisorbed state are similar to the ke-vve and kvv in the gas. The $V\pi^*$ component is similar to

imated in Fig. 4(b) by the Ni L_3 VV Auger line shape. Although the latter two components are facilitated through an intra-atomic $V\pi^*$ and $\pi^*\pi^*$ Auger process, respectively, they ultimately appear inter-atomic in character because one or both holes ultimately end up on the substrate [63].

The relative intensities of the three components can be understood within the final state rule. The electronic configuration per carbon atom in the ground state of chemisorbed ethylene, assuming charge neutrality, is nominally $\sigma^2\pi^{-1}\pi^*\pi^*$, where the π indicates the π bonding and π^* back-bonding charge transfer involved in the interaction with the metal substrate. Upon creation of the core hole, we expect that the valence electronic configuration assuming charge neutrality, becomes $\sigma^2\pi^*\pi^*$ or $V\pi^*\pi^*$, where y is the net charge transfer in the presence of the initial core hole. The relative intensities of the components, VV: $V\pi^*$: $\pi^*\pi^*$ should then be $16:8y:y^2$, or upon including the P_{III} matrix elements $13:7y:y^2$. Best agreement with the results obtained from the fit to the experimental line shapes (56:34:10, total normalized to 100) is obtained when $y = 1.3$, which gives relative intensities of 55:38:7 [63]. The 1.3 total electron transfer is consistent with the 1.3 core hole screening electrons found in benzene as determined from ab-initio theoretical calculations [64].

Similar interpretations of the Auger line shapes for ethylene/Ni at different temperatures have been reported by Ramaker *et al.* [63, 65]. Most interesting of these results is the evidence that the line shape at 600 K is not representative of a true carbide, since considerable C-C bonding character is reflected in the line shape. Similar C KVV Auger data reported by Caputi *et al.* reveal further changes in the line shape around 620 K [66]. Quantitative interpretations of these data suggest that the amount of C-C bonding character decreases at this temperature [65]. Recently, CEELS data has shown that the C-C bonding below 600 K corresponds to C_s (n mostly equal to 2) horizontally bonded to the surface, and that above 620 K a significant fraction of the C_s dissociates; however, at high coverages, some of the C_2 's flip up vertical to the surface [67]. Comparison with theoretical calculations [68] and additional experimental data indicate that these vertical C_2 's serve as precursors to the graphite nucleation sites [67].

6. Summary and thoughts for the future

In summary, the chemical effects seen in the various experimental C KVV line shapes do not arise from one-electron effects, but rather from many-body correlation and screening effects. This is apparent because the DOS self-folds are very similar to each other, in contrast to the experimental line shapes which reveal significant differences. Thus the differences seen between graphite and diamond for example result because diamond has just the σ orbitals with a single ΔU , graphite has both σ and π orbitals with different ΔU 's for the $\sigma\sigma$, $\sigma\pi$ and $\pi\pi$ holes. The differences between benzene, diamond, and C_{60} arise primarily from the different satellite magnitudes present. On the other hand, the hole-hole correlation and repulsion effects are much diminished for chemisorbed systems because of metallic screening from the substrate. In the chemisorbed case, and only in this case, the C KVV Auger line shape reflects the DOS self-fold

The review above of several areas where Auger line shape interpretation has provided considerable insight into localization, charge transfer, polarization, and screening processes should convince many readers that the results obtainable from this approach are worth the effort. However, Auger line shape analysis has not realized its full potential because a quantitative interpretation is still a formidable task in view of the many simultaneous processes and the many-body effects reflected in the total line shape. Indeed, often just the extraction of the line shape (i.e. removal of the background and inelastic losses) is not an easy task.

One way to simplify these two tasks is to limit the number of variables or to limit the number of simultaneous processes. I believe this is the direction of the future for AES, and that much progress will be made in this area in the coming years. The background and magnitude can be controlled by positron induced AES, PAES [69-71] and coincident techniques (Auger-photoelectron coincidence spectroscopy, APECS [72]). The latter technique also controls the initial state which controls the magnitude of the initial state satellites. A second way of controlling the initial state is by utilizing a tunable photon source, such as a synchrotron, to resonantly excite a core electron into a bound state (i.e. via de-excitation electron spectroscopy, DES [73]). By measuring the spin polarization of the Auger electrons one gains additional information about the possible process which caused them [74]. Spin polarized AES (SPAES) thus has two aspects; namely it assists in interpreting the normal $N(E)$ spectra and it has the potential to provide useful information in surface magnetism. Strong angular variations in the Auger line shapes of adsorbed molecules have also been observed [75, 76]. These angular variations are of significant help in determining the correct assignment of some of the fine structure in the line shape.

We know that the Cini expression will continue to be used on a wide variety of systems; even in the event of some progress in developing a theory for unfilled and degenerate bands. But much further work is needed to learn of its limitations and validity for a wider variety of materials.

Most Auger line shape interpretations to date have been on homogeneous solids, molecules, or at least on well characterized surfaces. And most interpretation schemes in the past require a one-electron DOS, which is then utilized to generate a self-fold for insertion into the Cini expression. The DOS are normally obtained empirically as described above. But the future will demand a study of more complex practical systems. As the technology moves to more complex "engineered" inhomogeneous materials such as multi-elemental alloys, composites, matrices, high temperature superconductors, and interfaces, AES is going to be increasingly useful because of its ability to sample a site or element specific local DOS. Thus, the future of AES is bright, but the theory must advance to be able to handle these increasingly complex systems. Much work remains to be done.

Acknowledgements

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